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Aberdeen Proving Ground, MD 21010-5424

ECBC-TR-1127

FATE OF THALLIUM(I) IN REVERSE OSMOSIS AND CHLORINATED WATER MATRICES

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The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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14. ABSTRACT:
This is the final report for a limited thallium fate study in support of the Joint Chemical Biological Radiological Agent Water Monitor program funded by the Defense Threat Reduction Agency. The persistence of thallium(I) sulfate in water prepared using reverse osmosis (RO) and RO water with added chlorine (RO-Cl) was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) for a period of 2 weeks. The depletion of thallium(I) from the solution occurred with half-lives of 116 and 131 days for the RO and RO-Cl solutions respectively; this depletion is assigned to the adsorption of thallium(I) on the walls of the vials that were used.

15. SUBJECT TERMS
Thallium | Thallium sulfate | Reverse osmosis | Chlorine water

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PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency (DTRA) project no. CA07DET122. The work was started in April 2010 and completed in December 2011.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgments

The authors thank Ngai Wong (DTRA) for his program management and funding support. The authors also thank Alan W. Zulich and Cynthia R. Swim, U.S. Army Edgewood Chemical Biological Center for administrative support and Carol Brevett (Science Applications International Corporation, Gunpowder, MD) for assistance with the manuscript formatting and editing.

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FATE OF THALLIUM (I) IN REVERSE OSMOSIS AND CHLORINATED WATER MATRICES

1. INTRODUCTION

The Joint Chemical Biological Radiological Agent Water Monitor (JCBRAWM) program is sponsored by the Defense Threat Reduction Agency (DTRA) to evaluate technologies capable of detecting threats deployed against water supplies. The Joint Services require early monitoring against chemical, biological, and radiological (CBR) contaminants in water for three missions: source site selection, treatment verification, and water quality during storage and distribution. The early warning monitor should rapidly and accurately detect and identify a CBR agent over a range of operational conditions.[1,2] In this report, the persistence of thallium(I), Tl^+, is measured.

Thallium(I), Tl^+, is a slow acting, cumulative poison. Thallium is extremely toxic by ingestion, with an oral LD50 in rats of 16 mg/kg,[1] and very toxic by skin absorption. Before the toxicity was understood, thallium was used as a rat poison and an ant bait. Thallium is not registered as a pesticide in the United States. Once ingested thallium acts by mimicking Na^+ and K^+ in cells and reacting with S-based moieties, such as cysteine. Thallium was a favorite poison of the Saddam Hussein regime in Iraq and was used against humans.[2]

The work reported herein represents a study on the fate of thallium(I) sulfate, Tl_2SO_4, dissolved in reverse-osmosis (RO) water and RO water supplemented with 2 ppm chlorine (Cl). In an attempt to prevent the salt from adsorbing onto the plastic vial container walls, siliconized (low-retention) screw-cap microfuge tubes were used. Without salt adsorption, it is expected that the thallium would remain in solution and be at a constant dissolved concentration for the entirety of the testing protocol.

2. EXPERIMENTAL PROCEDURES

2.1 Reagents

The thallium was obtained in the form of $T1_2SO_4$ (CAS number 7446-18-6, also called thallous sulfate) from Sigma-Aldrich Chemical Company (St. Louis, MO, item 88290-G). The structure for $T1_2SO_4$ is shown in Figure 1.

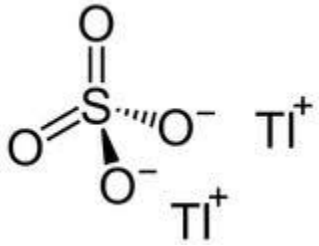

Figure 1. Schematic of thallium(I) sulfate

The RO water was prepared by running regular tap water through an Osmo 23G RO system (GE Osmonics, Minnetonka, MN) RO unit and was the same as in previous projects.[3,4]

The RO-Cl water was prepared by adding sodium hypochlorite (NaOCl) to the RO water to a final concentration of 2 ppm free chlorine as measured with a Hach AquaChek TruTest digital test strip reader (Hach Company, Elkhart, IN). The NaOCl solution was obtained from Sigma-Aldrich Chemical Company, item 425044-250ML, batch 09113ME, reagent grade, with 10–13% available chlorine. First, Dilution 1 was prepared by adding 50 µL of the Sigma-Aldrich NaOCl solution to 20 mL of RO water. A 2.74 mL aliquot of Dilution 1 was added to 7.26 mL of RO to prepare Dilution 2. Finally, 1.90 mL of Dilution 2 was further diluted with a total of 9.15 mL of RO to give a final concentration of 2.2 ppm as measured with the TruTest reader (average based on three measurements ranging from 2.0–2.3). The pH, based on an average of three measurements, was 6.6 for RO and RO-Cl water.

2.2 Instrumental Parameters

The concentration of thallium was measured using an inductively coupled plasma optical emission spectroscope (ICP-OES) model Optima 4300DV, manufactured by PerkinElmer, Waltham, MA (see Table for parameters). The method used was based on the procedures found in Internal Operating Procedure (IOP) MT-43, Revision 2 (see Appendix A).

Table. ICP-OES Parameters

SPECTROMETER PARAMETERS	
Purge Gas Flow: Normal	Resolution: Normal
Spectral Profiling: No	Read Time Delay: 60 s
Replicates: 3	Read Time: Auto
Min Time: 1 s	Max Time 5 s
PLASMA PARAMETERS	
Source Equilibration Delay: 3 s	Auxiliary Flow: 0.2 L/min
Plasma Flow: 15 L/min	Power Watts: 1300
Nebulizer Flow: 0.80 L/min	Plasma View: Axial
View Dist: 15.0	Sample Flow Rate: 1.50 mL/min
DETECTOR PARAMETERS	
Peak Algorithm: Peak Area	Points per Peak: 3
Overlap Correction: None	Background Correction: 2-Point
Internal Standard: Sc or Y	

2.3 Sample Preparation

2.3.1 Thallium(I) in RO-Cl Water

Tl_2SO_4 was dissolved in 1000 µL RO-Cl water to give a stock solution of approximately 5.2 mg/mL. This stock solution was then diluted with RO-Cl to a solution of approximately 200 µg/mL Tl^+ for incubation at 25 ºC. These samples are referred to as RO-Cl thallium incubation samples. Duplicate thallium incubation samples were prepared, each has a total volume of 1.400 mL. Twenty-five microliter aliquots of an incubation sample were removed at time points up to 37 days from initiation of incubation. Immediately upon removal from incubation, a 25 µL aliquot was diluted to 50 mL with RO water in a volumetric flask for ICP-OES analysis. A total of three replicate aliquots were removed from the incubating samples (to yield three replicate 50 mL ICP samples) at each time point. Each 50 mL ICP-OES sample was passed through a 0.45 µm filter, acidified to 10% acid with concentrated HNO_3, and analyzed by ICP-OES, in accordance with IOP MT-43 Revision 2 (see Appendix A) Section 7.1.4 (Liquid Samples – Dissolved Solids) of the IOP. The ICP-OES instrument was used to measure each sample three times and reports the mean found concentration. All thallium incubation samples had reportable amounts of thallium based on the ICP-OES analysis. The initial Tl^+ concentration was taken to be the value determined by ICP-OES at time zero because the Tl_2SO_4 stock was not prepared volumetrically.

Blank solutions were prepared in the same manner but were not spiked with thallium. Aliquots of thallium and blank were analyzed at the same time. The samples were incubated at 25 ºC in siliconized plastic screw-cap microfuge tubes (Fisher Scientific, Pittsburgh, PA, item 02-681-341) in a Fisher Scientific dry bath incubator.

2.3.2 Thallium(I) in RO Water

Samples were prepared and analyzed in a manner similar to that for thallium(I) in RO-Cl water (Section 2.3.1). Tl_2SO_4 was dissolved in 1000 µL RO water to give a stock solution of approximately 2.4 mg/mL. This stock solution was then diluted with RO to yield a solution of approximately 200 µg/mL Tl^+ for incubation at 25 ºC; these samples were referred to as RO thallium incubation samples. Duplicate thallium incubation samples were prepared, each in a total volume of 1.400 mL. Twenty-five µL aliquots of an incubation sample were removed at time points up to 36 days from initiation of incubation. Immediately upon removal from incubation, a 25 µL aliquot was diluted to 50 mL with RO water in a volumetric flask for ICP-OES analysis. ICP-OES analysis was carried out in the same manner as that performed for thallium(I) in RO-Cl water (Section 2.3.1).

Blank solutions also were prepared in the same manner but were not spiked with thallium. Water matrices free of thallium (blanks) were used as reference samples. Aliquots of thallium and the blanks were analyzed at the same time. The samples were incubated at 25 ºC in siliconized plastic screw-cap microfuge tubes (Fisher Scientific, item 02-681-341) in a Fisher Scientific dry bath incubator.

3 RESULTS

3.1 Thallium(I) in RO-Cl Water

Figure 2 presents a first-order kinetics plot of the concentration of Tl^+ in a solution of 2 ppm chlorine in RO water over a period of 888 h (37 days). An initial measured concentration of 100 µg/L (in the 50 mL analytical ICP-OES aliquot) declined to approximately 79 µg/L after 37 days, representing a loss of about 20% of the dissolved Tl^+ cation. The first-order half-life for depletion was 131 days. Representative ICP-OES data is provided in Appendix B.

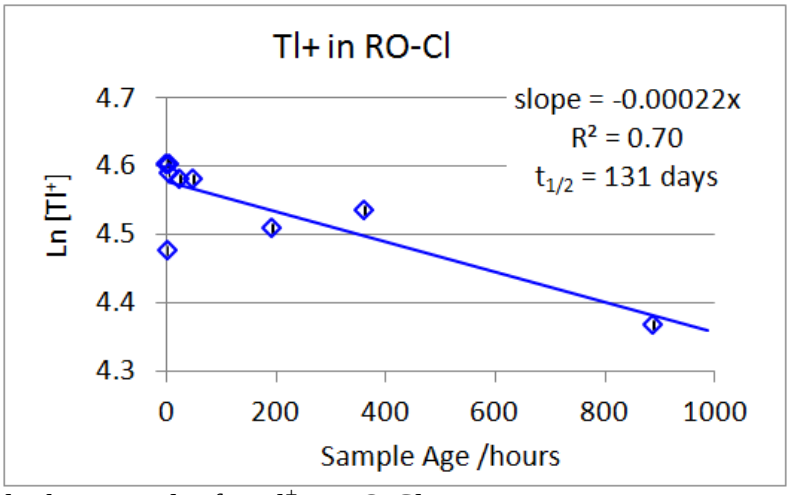

Figure 2. First-order kinetics plot for Tl^+ in RO-Cl water.

3.2 Thallium(I) in RO Water

Figure 3 presents a first-order kinetics plot of the concentration of Tl^+ in a solution of RO water over a period of 864 h (36 days). An initial measured concentration of 110 µg/L (in the 50 mL analytical ICP-OES aliquot) declined to approximately 91 µg/L after 36 days representing a depletion of about 17% of the dissolved Tl^+ cation. The first-order half-life for depletion was 116 days.

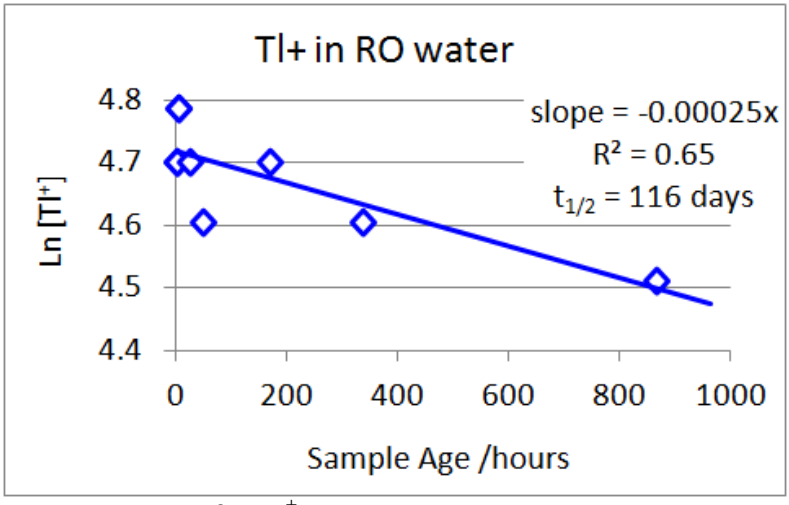

Figure 3. First-order kinetics plot for Tl^+ in RO water.

4. DISCUSSION

Data on the aqueous chemistry of thallium(I) are sparse and are not in agreement. The equations for the dissociation of Tl_2SO_4 into Tl^+ cation and SO_4^{2-} anion when dissolved in water are shown (eqs 1–3), and the formula for the stability constant of $TlSO_4^-$, β_1 is given (eq 4).

A prior study found that evidence for the existence of the ion $TlSO_4^-$ in solution was inconclusive.[5] Glaser gives the stability constant, β_1 for the formation of $TlSO_4^-$ in 2 M aqueous sodium perchlorate solution as 2.2,[6] and states that Tl^+ is only weakly hydrated in aqueous solution, and has a low tendency to form complexes. Another reference states that many Tl^+ salts show signs of being associated in solution.[7] This reference also reports a pK_a of 13 for aquated Tl^+, and that the precise nature of the hydrated ion in solution is not well established.[7] No further reactions of the Tl^+ are expected to occur in the aqueous conditions used in this study.

$$Tl_2SO_4 \leftrightarrows Tl^+ + TlSO_4^- \quad (1)$$

$$TlSO_4^- \leftrightarrows Tl^+ + SO_4^{2-} \quad (2)$$

$$Tl_2SO_4 \leftrightarrows 2\,Tl^+ + SO_4^{2-} \quad (3)$$

$$\beta_1 = [TlSO_4^-]/[Tl^+][\,SO_4^{2-}] = 2.2 \quad (4)$$

However, the measured loss of Tl^+ may be viewed as arising from a physical phenomenon. Because of the nature of the vial containing the thallium salt solution, it may be that loss of thallium concentration was a result of adsorption of Tl^+ on the vial walls. Plastic vials are known to have significant adsorption properties, especially for transition metal ions.[8] One

possible reason for the decrease in Tl^+ concentration may have been its adsorption to the walls of the vials, despite the fact that siliconized vials were used to try to avoid this problem.

5. CONCLUSIONS

The work reported herein represents a study on the fate of Tl_2SO_4 dissolved in RO water and RO water supplemented with 2 ppm chlorine (RO-Cl). In an attempt to prevent the thallium ions from adsorbing onto the plastic vial container walls, siliconized (low-retention) screw-cap microfuge tubes were used. The thallium sulfate solution displayed depletion half-lives of 116 and 131 days in RO and RO-Cl water solutions, respectively, for what is believed to be adsorption of Tl^+ onto the walls of the vial, despite the use of siliconized microfuge tubes.

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ACRONYMS AND ABBREVIATIONS

Cl	chlorine
DI	deionized water
ICP-OES	inductively coupled plasma optical emission spectroscopy
IOP	internal operating procedure
HCl	hydrochloric acid
HNO_3	nitric acid
LC	liquid chromatography
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
RO	reverse osmosis
Tl_2SO_4	thallium sulfate

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APPENDIX A

Internal Operating Procedure (IOP) MT-43, REVISION 2

Internal Operating Procedure: Directorate of Program Integration

Environmental Monitoring Laboratory

Title: Metals Analysis in the Laboratory Using Inductively-Coupled Plasma Optical Emission Spectrometry

Division: Operations

Branch: Environmental Monitoring Laboratory

Building: E-3330/Room 183, PBCA, or Field Location

This internal procedure covers operations, methods, and procedures of a general nature not covered by a standing operating procedure. This procedure will be effective until rescinded or superseded.

Changes to this procedure will be accomplished by submission of revisions or amendments.

Originator	Brandon E. Dusick	3/25/2010 Date
Analytical Team Leader	John Schwarz	3/29/10 Date
Quality Assurance Coordinator	Paul Stewart	3-29-10 Date
Environmental Monitoring Laboratory Chief	Steven D. Norman	3/25/10 Date

Date: March 25, 2010

IOP Number: MT-43

Revision Number: 2

Prepared by: Jill M. Meuser (410) 436-6731 Brandon Dusick (410) 436-5407

Approved by: Steven D. Norman (410) 436-8428

Scanned 3/24/10

Record of Change Page

Revision 2: Change liquid aliquot from 2 mL to 25 mL.
Change % acid of prepared standards to match % acid of samples.
Update liquid procedure to reflect analysis for dissolved elements in accordance with EPA SW-846.
Add QC Summary Chart.

Revision 1: Add reference to MBFORM-95 and MBFORM-96 for total arsenic reporting at PBCA. Update names of organizational units.

Revision 0: Initial preparation

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Signature Page

Title: Metals Analysis in the Laboratory Using Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Operator's Statement: I have read, or have had read to me, the procedures in this IOP. I, by my signature below, indicate that I thoroughly understand and agree to abide by these instructions.

Name (print)	Signature	Date

Supervisor's Statement: I have personally reviewed this IOP and, to the best of my knowledge, believe that the information listed herein is correct.

Supervisor: Steven D. Norman Date: 3/25/10

Steven D. Norman

Metals Analysis in the Laboratory Using Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES)

1.0 PRINCIPLE OF ANALYSIS

1.1 The Inductively-Coupled Plasma Optical Emission Spectrometer (ICP-OES) performs multi-element determinations on solutions using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of this method is atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol produced is transported to the plasma torch where excitation occurs. Element-specific emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by an echelle grating spectrometer designed to use multiple diffraction orders. To separate the orders and create a two-dimensional diffraction pattern, the echelle grating polychromator is combined with a cross-dispersing element. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position of the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.0 SCOPE

2.1 This IOP illustrates the determination of metals in various matrices by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES).

2.2 Samples require digestion unless constituents are completely dissolved, acidified, and filtered. This method is limited to metals in solution or solubilized through some form of sample processing. Due to the variability and complexity of sample matrices, preliminary treatment is necessary. Sample treatment process varies according to the matrix and the nature of the sample to be analyzed.

2.3 Detection Limits are dependent on the viewing mode (axial or radial), the accessories used, the degree of electrical expansion of the output signal, and the sample matrix. Method Detection Limits (MDLs) will vary and must be established for each target analyte and matrix individually.

2.4 Use of this method is restricted to analysts who are knowledgeable in the use of the ICP-OES and the quality assurance/quality control (QA/QC) required to produce valid analytical results. Additionally the analyst must be skilled in the interpretation of spectral and matrix interferences and the procedures used for their correction.

3.0 INTERFERENCES

3.1 A background correction technique should be used to compensate for background contributions but should not degrade the analytical result.

3.2 Chemical, spectral, physical, and memory interference effects may contribute to inaccuracies in the determination of trace metals by ICP.

3.2.1 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects, and are highly dependent on matrix type and specific target element. Such effects are not common, but if observed, can be minimized by careful selection of operating conditions.

3.2.2 Spectral interferences could be caused by, but not limited to: spectral overlap from another element; unresolved overlap of molecular band spectra; stray light from the line emission of high concentration elements; or background emission from continuous or recombination phenomena. Inter-element correction factors (IECs) are required to compensate for spectral overlap. Determination of IECs and use of spectral interference check solutions must be used in accordance with Section 3.1 of USEPA SW-846 Method 6010B. Samples should be treated using successive dilutions or internal standards in lieu of the method of standard addition if analyst should find continuing interference effects.

3.2.3 Physical interferences are effects associated with sample transport, nebulization, and conversion within the plasma. Physical interferences may be caused by high dissolved solids, high acid concentrations, or other conditions described in Section 3.2 of USEPA SW-846 Method 6010B. Such effects must be reduced in accordance with Method 6010B or the instrument manufacturer's instructions. The most common approach is dilution of the sample digestate, although a high solids nebulizer may be advisable if many samples with high dissolved solids are expected.

3.2.4 Memory interferences may result when analytes in a previous sample contribute to the signals measured in a new sample. Such interference must be identified and corrected, generally by establishing suitable rinse times to reduce analyte signals to within a factor of two of the MDL.

3.3 Instrument manufacturer's instructions and reference methods as listed in Section 15 must be followed to ensure that the many possible interferences are minimized.

4.0 DEFINITIONS

4.1 Calibration Blank/Instrument Blank – 10% standard dilution of nitric acid from which the calibration standards are made; solution analyzed to demonstrate lack of system contamination.

4.2 Calibration Standards – Serial dilutions made from the stock solution of the target analyte and 10% standard nitric acid solution. These standards are then for instrument optimization and determination of the relationship between instrument response and concentration (calibration).

4.3 Continuing Calibration Verification (CCV) Standard – Solution used to verify the continuing validity of the instrument calibration throughout the analysis. Analyzed after the ICV, every ten samples, and at the end of the analysis.

4.4 Dissolved Metals – Analytes measured in a sample acidified to a pH <2 and filtered through a 0.45 µm membrane.

4.5 Initial Calibration Verification (ICV) Standard – Solution that is prepared from a separate standard source from that used for calibration standards; analyzed immediately after the calibration curve to ensure preciseness and accuracy.

4.6 Laboratory Control Sample (LCS) – An aliquot of deionized water, QC sand, or other clean matrix representative of the matrix being analyzed, introduced in the laboratory, to which a known quantity of the analytes of interest are added and taken through each step of the sample preparation and analysis process.

4.7 Laboratory Control Sample Duplicate (LCSD) – A second LCS, as described above.

4.8 Method Blank – Also called a Matrix Blank, a sample that contains reagents used in the process as well as the matrix of the samples, all in the same volumes and concentrations as used for the samples.

4.9 Suspended Metals – Analyte(s) in the material retained by a 0.45 µm membrane.

4.10 Total Metals – Analyte(s) determined on an unfiltered sample following vigorous digestion.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the sample preparation chemist to ensure that all preparation steps conform to the protocol in this procedure. Any deviations from this method must be approved by the Branch Chief or a designee prior to analysis and documented including a discussion of reasoning.

5.2 It is the responsibility of the operator to ensure that all steps involved in the sample analysis, after the completion of sample preparation, conform to the standards outlined in this procedure. Any deviations from this method must be approved by the Branch Chief or a designee prior to analysis and documented including a discussion of reasoning.

5.3 It is also the responsibility of the operator to become familiar with the information provided in the MSDS for each chemical used in this procedure.

6.0 REQUIREMENTS

6.1 Equipment

6.1.1 Computer-controlled inductively-coupled plasma optical emission spectrometer with background correction.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Optional mass-flow controller for argon nebulizer gas supply.

6.1.4 Optional peristaltic pump.

6.1.5 Autosampler.

6.1.6 Computer with appropriate software.

6.1.7 Water chiller/recirculator.

6.1.8 Hotblock apparatus at 95°C, calibrated with thermometer.

6.1.9 Assorted pipettes, beakers, and watch glasses.

6.1.10 Digestion vessels and caps, 50 mL.

6.1.11 Sample vessels and caps, 15 mL

6.1.12 Glassware – volumetric flasks of suitable precision and accuracy. To ensure that glassware is clean and contaminant free it should be washed in the following sequence: 1:1 nitric acid, tap water, detergent, tap water, and reagent water.

6.1.13 Forceps.

6.1.14 Air Sampler: Cellulose ester membrane filter.

6.1.15 Wipe: moist disposable towel meeting ASTM E1792 that dissolves during digestion.

6.1.16 A sample pump capable of drawing 1 – 4 liters of air per minute with flexible tubing.

6.1.17 Argon gas supply – high purity grade (99.996%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders. (80 – 120 psig).

6.1.18 Nitrogen gas supply for purge gas**.**

6.1.19 Air – Compressed air – (80 – 120 psig) for shear gas.

6.2 Reagents

6.2.1 Nitric acid, conc., trace metal grade, ultra pure.

6.2.2 Nitric acid, 1:1, trace metal grade, ultra pure. Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker.

6.2.3 Hydrochloric acid, conc, trace metal grade.

6.2.4 Calibration stock solutions.

6.2.5 Distilled, deionized, Type II water.

6.2.6 Diluting/Standard solution: 10% HNO_3. To about 800 mL of DI water in a 1-L volumetric flask, slowly add 100 mL conc. HNO_3. Dilute to the mark with DI water.

6.2.7 Internal standard – The use of Scandium and/or Yttrium is strongly recommended for the determination of all analytes when using the ICP-OES. This will correct for general chemical interferences. Other modifiers may also be used as recommended by the instrument manufacturer or when interference is evident.

6.2.8 Analytical Reference Material. Standards of target elements, with certified concentrations traceable to NIST-certified standards. These solutions can be purchased from many suppliers. Two separate standards for each metal (one for Calibration and the other for ICV, CCV, and spiking) are required; purchase from different companies is recommended.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 CE Filters

7.1.1.1 Open cassette filter and place filter in 50-mL conical vial.

7.1.1.2 Open an unused cassette filter and place filter in 50-mL conical vial as a method blank.

7.1.1.3 Open two unused cassette filters and place each filter in a conical vial for LCS and LCSD and spike appropriately with all target analytes.

7.1.1.4 Add 1.25 mL of concentrated HCl to the sample.

7.1.1.5 Place in the hot block digester and heat at 95°C for 15 minutes covered loosely with the vial cap.

7.1.1.6 Remove and cool for 5 minutes.

7.1.1.7 Add 1.25 mL of concentrated HNO_3 to the sample and return to heat for 15 minutes.

7.1.1.8 Cool samples and bring up to a final volume of 25 mL with DI water.

7.1.2 Wipes

7.1.2.1 Place wipe samples in pre-labeled 50-mL conical vials if not already stored in vials.

7.1.2.2 Place an unused wipe in a 50-mL conical vial as a method blank

7.1.2.3 Place unused wipes in 50-mL conical vials for LCS and LCSD samples and spike appropriately with all target analytes.

7.1.2.4 Add 1.25 mL of concentrated HCl to each vial.

7.1.2.5 Place in the hot block digester and heat at 95°C for 15 minutes, covered loosely with the vial cap.

7.1.2.6 Remove and cool for 5 minutes.

7.1.2.7 Add 1.25 mL of concentrated HNO_3, cover, and return to heat for 15 minutes.

7.1.2.8 Cool samples and bring up to a final volume of 25 mL with DI water.

7.1.3 Liquid Samples - Digestion

7.1.3.1 Measure 25 mL of the sample into a conical vial.

7.1.3.2 Measure 25 mL of reagent water into a conical vial as a method blank.

7.1.3.3 Measure 25 mL of reagent water for LCS and LCSD and spike appropriately with all target analytes.

7.1.3.4 Add 5 mL of 1:1 HNO_3 to the sample, mix gently, and cover loosely with conical vial cover.

7.1.3.5 Heat sample at 95°C and reflux for 10 minutes without boiling.

7.1.3.6 Allow to sample to cool.

7.1.3.7 Add 2.5 mL of concentrated HNO_3, cover, and return to heat for 30 minutes.

7.1.3.8 If brown fumes are observed, repeat previous step not to exceed 5 mL.

7.1.3.9 Allow samples to cool.

7.1.3.10 Add 2 mL of DI water, cover, return to heat, and reflux for 2 hours at 95°C without boiling.

7.1.3.11 Add 5 mL of concentrated HCl, cover, and return to heat for 15 minutes.

7.1.3.12 Allow to cool and bring up to 50 mL final volume with DI water.

7.1.4 Liquid Samples – Dissolved Solids

7.1.4.1 Samples should be received having been filtered in the field through a 0.45 µm filter, then acidified with 5 mL concentrated HNO_3 per liter of sample.

7.1.4.2 For the method blank, filter reagent water through a 0.45 µm filter.

7.1.4.3 For the LCS and LCSD spike reagent water with target analytes at the target concentration then filter the water through a 0.45 µm filter.

7.1.4.4 For the MS and MSD, spike two aliquots of sample water with target analytes at the target concentration

7.1.4.5 Measure 13.5 mL of the MB, Sample, MS, MSD, LCS, and LCSD into a 15mL vessel.

7.1.4.6 Add 1.5 mL of concentrated HNO_3 to each analytical aliquot. If the sample, MS, or MSD was preserved with more acid that indicated in 7.1.41., adjust the volume of concentrated HNO_3 to achieve 10% acid concentration.

7.1.4.7 Mix thoroughly and analyze.

7.1.5 Solid Samples

7.1.5.1 Measure 2 grams of the sample into a conical vial.

7.1.5.2 Measure 2 grams of QC sand into a conical vial as a method blank.

7.1.5.3 Measure 2 grams of QC sand for LCS and LCSD and spike appropriately with all target analytes.

7.1.5.4 Add 5 mL of 1:1 HNO_3 to the sample, mix gently, and cover loosely with conical vial cover.

7.1.5.5 Heat sample at 95°C and reflux for 10 minutes without boiling.

7.1.5.6 Allow to sample to cool.

7.1.5.7 Add 2.5 mL of concentrated HNO_3, cover, and return to heat for 30 minutes.

7.1.5.8 If brown fumes are observed, repeat previous step not to exceed 5 mL.

7.1.5.9 Allow samples to cool.

7.1.5.10 Add 2 mL of DI water, cover, return to heat, and reflux for 2 hours at 95°C without boiling.

7.1.5.11 Add 5 mL of concentrated HCl, cover, and return to heat for 15 minutes.

7.1.5.12 Allow to cool and bring up to 50 mL final volume with DI water.

7.2 General Instrument Set-up

7.2.1 Ensure that all necessary gases are present and gas pressures are appropriate. Appropriate pressure settings are as follows:
Air, 25 L/min
Argon, 80 – 120 psig
Nitrogen, 50 psig

7.2.2 Ensure that the cooling system has enough water (distilled water must be used).

7.2.3 Ensure that there is no moisture or condensation in the air line going to the instrument. Failure to do so will have fatal results to the instrument.

7.2.4 Fill rinse container with 1% v/v nitric acid.

7.2.5 The main instrument switch should be on at all times with a constant flow of liquid Argon.

7.2.6 Turn computer on and open instrument software. Instrument will go through startup procedure.

7.2.7 After the software completes the Diagnostic Cycle, the plasma should be turned on using the software. The analyst must wait half an hour for the system to stabilize before running samples.

7.3 Calibration

7.3.1 In WINLAB, go into Workspace, open windows.

7.3.2 Set up a calibration curve in the Method Editor portion of the software or select an existing method. The curve will typically span 10 to 100 ppb (µg/L). There should be at least five points used to acquire the calibration curve

7.3.3 Select the Automated Analysis Control icon on the tool bar and choose calibrate.

7.3.4 The regression calculation will generate a Correlation Coefficient (r^2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.000 indicates a perfect fit. The Correlation Coefficient of the calibration curve must be greater than or equal to 0.990 to be acceptable.

7.3.5 The y-intercept must be calculated from the regression; it may not be forced through the origin.

7.4 Analysis

7.4.1 Select the Sample Information Editor on the tool bar to enter sample information.

7.4.2 Go to the Automated Analysis Control icon on the tool bar and, under set up, create a sequence.

7.4.3 Run the sequence by going to the Analysis window and selecting Analyze Samples.

7.5 Shutdown

7.5.1 Flush sampler with DI water.

7.5.2 Remove sample probe and tubing from rinse run pump to dry out rinse in system.

7.5.3 Turn off plasma.

7.5.4 Exit software.

7.5.5 Loosen the pressure applied to the tubing on the peristaltic pump.

8.0 WASTE AND HAZARDOUS MATERIALS

The waste stream will consist of various metal constituents dissolved in dilute nitric acid.

9.0 QUALITY CONTROL

A summary of Quality Control requirements is shown in Appendix C.

9.1 Determination of the Linear Calibration Range – The upper limit of the linear calibration range must be established for each analytical wavelength by determining the signal responses from a minimum of five different concentration standards across the range, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper Linear Dynamic Range (LDR) limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Measured sample analyte concentrations that are greater than 100% of the upper LDR limit must be diluted and reanalyzed.

9.2 Method Detection Limits (MDLs) must be established using a sample fortified at a concentration of two to five times the estimated detection limit. To determine the MDL values, take at least seven representative matrix aliquots of the same type that will be used during sampling, spike at the appropriate level, and process through the entire analytical method. MDLs and PQLs are calculated using the protocol described in 40 CFR 136 Appendix B.

9.3 Assessing Laboratory Performance

9.3.1 Calibration Blank/Instrument Blank – The laboratory must analyze a blank before the analytical sequence, after every 10 samples, and at the end of the analytical sequence. These samples demonstrate that interferences from the analytical system, glassware, and reagents are under control, and guard against chronic laboratory contamination. All calibration/instrument blanks must be free of target analytes to the MDL. If the acceptance criterion is not met, correct the problem, documenting findings and actions. Re-prepare and re-analyze calibration blank and samples since the previous acceptable blank.

9.3.2 Method Blank (MB) – A method blank is an aliquot of clean matrix, similar to the sample matrix, that is taken through all steps of the analytical protocol in the same manner as if it were a sample. The laboratory must analyze at least one method blank with each batch of 20 or fewer samples. The MB is used to assess possible contamination from the sample preparation procedure and to assess spectral background from the reagents used in the sample processing. For liquid and solid samples, if the MB contamination exceeds ½ the LOQ, the source of contamination must be found and eliminated. If blank contamination exceeds 1/10 the level found in any sample, all samples with detectable results must be reprocessed in a subsequent preparation batch. For CE filter and wipe samples the method blank is subtracted from the sample result in accordance with published protocols.

9.3.3 Laboratory control spike/laboratory control spike duplicate (LCS/LCSD) – LCS/LCSD samples are laboratory-spikes of two clean matrix samples, matching the sample type being submitted to the laboratory from the field. The laboratory must analyze at least one LCS/LCSD pair with each batch of 20 or fewer samples. The laboratory must establish control limits; typically control limits for bias (percent recovery) are based on the historical mean recovery plus or minus three standard deviation units and control limits for precision (relative percent difference, RPD) range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. If the percent recovery or RPD falls outside the control limits, the method is considered out of control and the source of the problem must be identified and resolved before continuing the analysis. After resolving the problem, samples analyzed under out-of-control conditions must be reanalyzed. Default control limits of 75% to 125 % recovery and 0% to 20% RPD shall be used until sufficient data (30 points) are generated to calculate laboratory-specific limits.

9.3.4 Instrument performance – For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration and standards, run the calibration blank, the ICV, and the CCV immediately following each calibration routine. Both the ICV and CCV must be verified within ± 10% of the true value with relative standard deviation < 5% from replicate integrations. If calibration cannot be verified within these limits, the cause must be determined and the instrument must be recalibrated.

To check if the instrument is properly calibrated on a continuing basis, run a CCV (mid point standard) and a calibration blank every ten samples and at the end of the sample run. The found concentration must be verified within ± 10% of the true value and relative standard deviation of replicate measurements on the same standard must be ≤ 5%. If the CCV result is outside the ± 10% range, rerun the CCV. If the second CCV percent recovery is greater than 110% and the target analyte was not detected in a sample, data up to the CCV may be reported although the instrument needs to be recalibrated before additional samples are analyzed. If the target analyte was detected and the second CCV percent recovery is greater than 110%, those samples with detections must be reanalyzed after recalibrating the instrument. Regardless of whether the target analyte was detected, if the second CCV percent recovery is less than 90%, all samples since the last acceptable CCV must be reanalyzed after recalibrating the instrument.

9.4 Assessing Analyte Recovery And Data Quality

Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data.

9.4.1 Matrix spike/matrix spike duplicate (MS/MSD) – MS/MSD samples are laboratory-spikes of two aliquots of a field sample. The laboratory must analyze at least one MS/MSD pair with each batch of 20 or fewer water or soil samples unless specified otherwise by the client. For matrix evaluation, the QC acceptance criteria for the LCS/LCSD of the same matrix are used. In-house MS/MSD limits will be established from at least 30 data pairs that can be used for insight concerning matrix effects.

If the recovery or RPD falls outside the control limits, the samples should be reanalyzed. If the results are again outside the control limits, and all other QC parameters are in control (e.g., calibration, blanks, LCS/LCSD), the nature of matrix is assumed to be affecting recovery. This effect should be discussed in the analytical report narrative.

9.4.2 For filter and wipe samples, it is not possible to obtain multiple aliquots of the same sample. For these sample types, no matrix spike/matrix spike duplicate are required.

9.4.3 If matrix effects are suspected, post-digestion spikes can be analyzed. Analyte should be added at a level equivalent to ten times the requested detection limit. In instances where this level will not be sufficient, the analyte is to be added at a level that is one half the concentration of the sample.

9.4.4 Other tests to resolve matrix issues include dilution tests and the method of standard addition. Details on these tests can be found in SW-846, Method 6010B.

9.5 Interelement and background correction factors must be verified at the beginning of each analytical run by analyzing the interference check sample. Results should be within ± 20% of the true value. If results are outside this limit for any target analyte, the cause must be investigated and corrected before continuing the analytical run.

10.0 CALCULATIONS

10.1 Calibration is achieved by performing a linear regression of the instrument response versus the concentration of the standards. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

where: y = Instrument response (peak area or height)
m = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = Y-intercept

The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. In calculating sample concentrations, the regression equation is rearranged to solve for the concentration (x), as shown below.

$$x = \frac{y - b}{m}$$

10.2 Dilution Factor (DF) is the final volume divided by the initial volume of solution, as shown below. When determining the DF, only dilution of the digestate is included. Do not include any factors related to digestion of the initial sample aliquot.

$$DF = \frac{V_i + V_b}{V_i} = \frac{V_f}{V_i}$$

where: V_i = volume in mLs of digestate used in the dilution
V_b = volume in mLs of acidified blank water used in the dilution
V_f = final volume in mLs of diluted digestate

For multiple dilutions, the dilution factor is the product of the dilution factors for each individual dilution. For example if 5 mL were dilution to 100 mL and 2 mL of the resulting solution was diluted to 50 mL, the dilution factor would be:

$$DF = \frac{100}{5} \times \frac{50}{2} = 20 \times 25 = 500$$

10.3 Water and Other Liquid Samples

10.3.1 All results for liquid samples are reported to two significant figures, in terms of the original sample. Results are generally in units of µg/L, but may be mg/L or %. Units must be consistent within a project.

10.3.2 Calculate the sample concentration as follows:

$$\mu g/L = \frac{R_i \times DF \times V_D}{V_S}$$

where: R_i = Instrument reading in µg/L
DF = Dilution factor, as described in Section 9.3.2
V_D = Final digestion volume in milliliters (mL)
V_S = Sample volume in milliliters (mL) used in the digestion

10.3.3 If any of the calculation factors have been included in the instrument software for reporting results, ensure that duplicate calculations do not occur.

10.4 Soil and Other Solid Samples

10.4.1 All results for solid samples are reported to two significant figures, in consistent units on wet weight basis. Units are generally µg/Kg or mg/Kg.

10.4.2 Calculate the sample concentration as follows:

$$\mu g/Kg = \frac{R_i \times DF \times V_D}{1000 \times W_S}$$

where: R_i = Instrument reading in µg/L
DF = Dilution factor, as described in Section 10.2
V_D = Final digestion volume in milliliters (mL)
W_S = Sample weight in grams (g) used in the digestion

10.4.3 If any of the calculation factors have been included in the instrument software for reporting results, ensure that duplicate calculations do not occur.

10.5 CE Filter Air Samples

10.5.1 Air sample data are reported to two significant figures in units of mg/m^3. If data are not available to calculate sample volume, results are reported on a per sample basis.

10.5.2 Calculating the sample concentration is a multi-step process, as follows:

10.5.2.1 If the actual sample volume (V_S) has not been provided, calculate the volume

Sample Volume (L) = Flow (L/min) x Sample Interval (min)

Either the volume or the flow and interval must be provided in order to calculate concentration.

10.5.2.2 Calculate the µg/sample in the media blank

$$M_b = \frac{R_i \times V_D \times DF}{1000}$$

where: M_b = Total analyte mass in the media blank (µg)
R_i = Instrument reading in µg/L
V_D = Final digestion volume in milliliters (mL)
DF = Dilution factor, as described in Section 10.2

10.5.2.3 Calculate the µg/sample in the sample

$$M_S = \frac{R_i \times V_D \times DF}{1000}$$

where: M_S = Total analyte mass in the sample (µg)
R_i = Instrument reading in µg/L
V_D = Final digestion volume in milliliters (mL)
DF = Dilution factor, as described in Section 10.2

10.5.2.4 Calculate the concentration of the target analyte in the sample:

$$C_S, mg/m^3 = \frac{M_S - M_b}{V_S}$$

where: C_S = Sample concentration
M_S = Total analyte mass in the sample (µg)
M_b = Total analyte mass in the media blank (µg)
V_S = Sample volume (L)

10.6 Wipe Samples

10.6.1 Wipe sample data should be reported in units of µg/cm^2 or mg/m^2. If the area wiped is not provided, results are reported on a per sample basis.

10.6.2 Calculating the sample concentration is a multi-step process, as follows:

10.6.2.1 Calculate the µg/sample in the media blank

$$M_b = \frac{R_i \times V_D \times DF}{1000}$$

where: M_b = Total analyte mass in the media blank (µg)
R_i = Instrument reading in µg/L
V_D = Final digestion volume in milliliters (mL)
DF = Dilution factor, as described in Section 10.2

10.6.2.2 Calculate the µg/sample in the sample

$$M_S = \frac{R_i \text{ x } V_D \text{ x } DF}{1000}$$

where: M_S = Total analyte mass in the sample (µg)
R_i = Instrument reading in µg/L
V_D = Final digestion volume in milliliters (mL)
DF = Dilution factor, as described in Section 10.2

10.6.2.3 Calculate the concentration of the target analyte in the sample:

$$C_S, \mu g/cm^2 = \frac{M_S - M_b}{cm^2}$$

or

$$C_S, mg/m^2 = \frac{M_S - M_b}{0.1 \times cm^2}$$

where: C_S = Sample concentration
M_S = Total analyte mass in the sample (µg)
M_b = Total analyte mass in the media blank (µg)
cm^2 = Area sampled (cm^2)

10.7 Percent recovery is reported for ICV, CCV, interference check sample, LCS/LCSD and MS/MSD. The recovery is calculated as follows:

$$\%R = \frac{\text{Found concentration}}{\text{True concentration}} \times 100$$

10.8 Relative percent difference (RPD) between spiked duplicate determinations is reported for LCS/LCSD and MS/MSD. RPD is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} \times 100$$

where: RPD = Relative percent difference
C_1 = First sample found concentration
C_2 = Second sample found concentration (replicate)

10.9 All data will be reported to two significant figures, as follows:

10.9.1 If the target analyte is detected at a concentration above the Limit of Quantitation (LOQ, i.e., the higher of the statistically-calculated PQL or the lowest calibration standard), the result will be reported.

10.9.2 If the concentration of the target analyte is below the current laboratory LOQ but above the laboratory Method Detection Limit (MDL), the concentration will be reported and flagged with the "J" qualifier.

10.9.3 If the target analyte is not detected or is detected at a concentration below the MDL, the results will be reported as "less than the LOQ" ("< [numerical value of LOQ]").

10.9.4 If the sample digestate required dilution after the initial preparation, the result will be qualified with a "D."

10.10 In laboratory notebooks, record lot number and manufacturer of concentrated standards used, how and when standards were prepared, how spikes were made, and how samples were prepared.

11.0 DATA REPORTING

In addition to the requirements set forth below, the laboratory at PBCA will report total arsenic concentrations for filters and wipes using MBFORM-95 and MBFORM-96, respectively. The analyst will ensure that the latest revision is used. Samples of the form are provided in Appendices A and B.

11.1 The analyst shall provide reports and other deliverables as specified in this section unless superseded in writing by a client-specified format. The required content and form of each deliverable is described in this section. All reports and documentation must be:

- Complete
- Legible, including handwriting and copies,
- Clearly labeled and completed in accordance with instructions in this section,
- Arranged in the order specified in this section,
- Properly corrected (handwritten corrections must be legible, initialed, and dated), and
- Free of White-out® and Post-It® notes or other items which are not allowed.

11.1.1 Prior to submission, the analyst shall arrange items and the components of each item in the order listed in these sections.

11.1.2 If samples from more than one client are analyzed in one batch, a separate complete package shall be prepared for each client. Information not related to the client receiving the report shall be removed, including sample designations for the MS/MSD pair in the batch.

11.1.3 If samples from more than one client are analyzed in one batch, all QC results will be copied and included in the package for each client.

11.1.4 If an analyte is manually adjusted in any sample, standard, or blank, the report for that analyte before and after manual adjustment shall be included. The technical reason why the analyte required manual adjustment shall be noted in such a manner that the judgment can be verified by an independent reviewer. The notation shall be initialed and dated by the analyst.

11.2 The Sample Data Package is divided into the eight major units described in this section. The Sample Data Package shall include data for the analyses of samples from one client, in one or more batches, including field samples, dilutions, re-analyses, instrument blanks, calibration, interference check, ICV, CCV, Method Blank(s), LCS/LCSD, and any requested or required MS/MSD. A blank, colored sheet of paper will separate sections.

11.2.1 Section 1

11.2.1.1 Narrative: This document shall be clearly labeled "ECBC Environmental Monitoring Laboratory Analytical Narrative" and shall contain at a minimum:

- Laboratory name
- Client/Project name
- ECBC sample numbers being reported
- Analytical batch number(s)
- Detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing the samples reported in the data package.
- Discussion of any IOP modification/variance.

11.2.1.2 Scratch Log, complete with analyst, instrument, date extracted, date analyzed, and sample results. After supervisor review, this is moved to Section 8 and the Analytical Results (Part 1) Report and Analytical QC Results (Part 2) Report (collectively MBFORM-41) are placed in this section. At PBCA, MBFORM-95 and MBFORM-96 will be included in Section 1.

11.2.1.3 Injection log covering the entire analytical sequence. If more than a single log is necessary, forms shall be arranged in chronological order by instrument.

11.2.1.4 Method Blank Summary. This form includes all QC, samples, dilution, and re-extractions associated with a method blank. If more than a single form is necessary, forms shall be arranged in chronological order by date of analysis of the blank, by instrument.

11.2.2 Section 2

11.2.2.1 Interference check sample verification from the beginning of each analytical run reported in the data package.

11.2.2.2 Initial calibration data and plots of linear regression shall be included in chronological order by instrument, if more than one instrument is used. Required items are standard(s) quantitation reports for the initial calibration regardless of which day the calibration was performed.

11.2.2.3 ICV and ICB data, if calibration was not performed on the same day(s) as the sample analyses being reported.

11.2.3 Section 3

Check Standards (CCV) data and evaluation report shall be included in chronological order by instrument, if more than one instrument is used.

11.2.4 Section 4

Matrix Spike/Matrix Spike Duplicate Recovery (MS/MSD) data and evaluation form. If more than a single form is necessary, forms shall be arranged in chronological order by date of analysis of the MS/MSDs, by instrument. The MS/MSD form must be followed by the quantitation report.

11.2.5 Section 5

Method, reagent, and instrument blanks in chronological order, by instrument.

11.2.6 Section 6

Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) data and evaluation form. If more than a single form is necessary, forms shall be arranged in chronological order by date of analysis of the blank, by instrument. The LCS/LCSD form must be followed by the quantitation report.

11.2.7 Section 7

Sample data, including dilutions, and re-analyses data, shall be arranged in packets with the quantitation report for all detected and non-detected target elements. The samples shall be placed in increasing Environmental Monitoring Laboratory sample number order, considering both letters and numbers. This may not correspond to the order in which the samples were analyzed.

11.2.8 Section 8

11.2.8.1 Chains of Custody and copies of digestion log book showing all samples in the data package.

11.2.8.2 Any other supporting data. For example, screening data, memos, notations, Scratch Logs used to create Analytical Results Reports.

11.2.8.3 MBFORM 71 showing the numbers for standards used for calibration and spiking. These numbers will be used to append data from the Standards Log to ensure that all standards are traceable.

11.3 Data and Report Formats

11.3.1 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the system must identify such edits or manual procedures. A hardcopy printout displaying the manual adjustment shall be included in the raw data. This applies to all target elements.

11.3.2 The analyst shall identify all samples, including dilutions and re-analyses, LCS/LCSD, MS/MSD, Method Blanks, and standards with a unique Environmental Monitoring Laboratory sample number.

11.3.2.1 For field samples, the Environmental Monitoring Laboratory sample number is the nine- or ten-character unique identifying number assigned at log-in to the MUD tracking system. The first three characters are letters designating the location of the laboratory. The next six characters are numbers assigned by the data system in sequential order. The final two or three characters are letters signifying the type of sample. In order to facilitate data assessment, the analyst shall use the following sample suffixes:

- AAAXXXXXX = EML sample number
- AAAXXXXXX-MS = Matrix spike sample
- AAAXXXXXX-MSD = Matrix spike duplicate sample
- AAAXXXXXX-RA = Re-analyzed sample
- AAAXXXXXX-RE = Re-extracted and re-analyzed sample
- AAAXXXXXX-DL = Sample analyzed at a dilution
- AAAXXXXXX-DL2 = Sample analyzed at a secondary dilution
- AAAXXXXXX-DL3 = Sample analyzed at a third dilution
- AAAXXXXXX-DUP = Sample duplicate

11.3.2.2 The Environmental Monitoring Laboratory sample number shall be unique for each blank and LCS/LCSD within a sample delivery group. The unique number will be the eight digit extraction batch number in the format YYMMDD6X, where YYMMDD is the day the digestion was performed and X is the sequential number representing each batch analyzed on that date. The MB, LCS, and LCSD number will be the batch number plus the appropriate suffix, as defined below:

- XXXXXXXX = extraction batch number
- XXXXXXXX-MB = Method blank
- XXXXXXXX-LCS = Laboratory control sample
- XXXXXXXX-LCSD = Laboratory control sample duplicate

11.3.3 Cross out unused columns and spaces. Initial and date all cross outs.

11.3.4 Do not use paper clips or staple pages together.

12.0 SAFETY CONSIDERATIONS

Safety glasses, gloves and lab coats are to be worn at all times. Safety shoes are to be worn when handling compressed gas cylinders. Care should also be taken when handling any acids.

13.0 REFERENCES

ASTM E 1644-94 Hot Plate Digestion of Dust Wipe Samples for the Determination of Lead by Atomic Spectrometry.

Boss, Charles B. and Freeden, Kenneth J. *Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry.* The Perkin-Elmer Corporation, Norwalk, CT. 1997.

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USEPA Office of Solid Waste, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. 3rd Edition, "Chapter 1 Quality Control," July 1992.

USEPA Office of Solid Waste, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. 3rd Edition, Methods 3005A, 3050B, and 6010B, December 1996.

USEPA Method 200.7. "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma – Atomic Emission Spectroscopy," Revision 4.4. May 1994.

Appendix A Sample of MBFORM-95

MBFORM-95
July 2008
Revision 0

PBCA Total Arsenic Results
Cellulose-Ester Filters

COC: DATE:

	Sample ID	Sample Description	Average Starting Flow (L/min)	Average Ending Flow (L/min)	Time On (hhmm)	Time Off (hhmm)	Reported Arsenic Conc. (µg/L)	Calculated Arsenic Conc. (mg)	Total Sample Time (min)	Air Volume Sampled (m^3)	Results (mg/m^3)
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											

NOTES:

The action level is 0.01mg/m^3 or 200 µg/L assuming that a 480 L sample was taken.
ND means Non-Detect and indicates that the data was less than the PQL of 24 µg/L or < 0.00125 mg/m^3.

Appendix B Sample of MBFORM-96

MBFORM-96
July 2008
Revision 0

PBCA Total Arsenic Results
Ghost Wipe™ Samples

COC #: DATE:

	Sample ID	Sample Description	Area Sampled (cm^2)	Reported Arsenic Conc. (µg/L)	Calculated Arsenic Conc. (µg)	Results (µg/cm^2)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

NOTES:

The action level is 0.038 ug/cm^2 or 152 ug/L assuming that a 100 cm^2 sample was taken.
ND means Non-Detect and indicates that the data was less than the PQL of 50 ug/L or < 0.01 ug/cm^2.

Appendix C Summary of Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Before using any test method and at any time there is a significant change in instrument type, personnel, or test method.	QC acceptance criteria for LCS/LCSD and MS/MSD.	Recalculate results; locate and fix problem, then rerun demonstration.	NA	This is a demonstration of analyst ability to generate acceptable accuracy and precision using four replicate analyses of a QC check samples (e.g., LCS). No analysis shall be allowed by analyst until successful demonstration of capability is complete.
MDL Study	At initial set-up and subsequently once per 12 months. Quarterly analysis of MDL verification check samples.	See 40 CFR 136 Appendix B. MDL samples must produce a signal at least 3 times the instrument noise level, at a concentration approximately 2 times the reported MDL.	Run MDL verification check at higher level and set MDL higher or reconduct MDL study.	NA	Samples cannot be analyzed without a valid MDL.
Initial Calibration (ICAL): Minimum 5 standards and a calibration blank	Before sample analysis, at any major change in analytical system, or after failing calibration verification.	$r^2 \geq 0.990$	Correct problem, documenting findings and actions; repeat initial calibration	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second Source Calibration Verification (ICV)	Once after each initial calibration, before sample analysis.	Value of second source within ± 10% of expected value (initial source).	Correct problem, documenting findings and actions; verify second source standards. Rerun ICV. If that fails, correct problem, documenting findings and actions; repeat initial calibration.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.

Appendix C Summary of Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing Calibration Verification (CCV)	At least every 10 samples and at the end of the analytical sequence.	Percent recovery between 90% and 110% of the expected value.	Rerun CCV. If result < 90%, repeat ICAL and re-analyze all samples since the last passing CCV. If result >110%, report samples with non-detects since last passing CCV, and repeat ICAL before analyzing more samples. If result >110%, repeat ICAL and re-analyze all samples with analyte detections.	Flagging criteria are not appropriate. However, apply Q flag if no sample material remains and analyte exceeds criteria.	No samples may be reported without a valid CCV.
Method Blank	One per preparatory batch, matching sample matrix.	No analyte detected > ½ LOQ and greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). For common laboratory contaminants, no analytes detected >LOQ.	Correct problem, documenting findings and actions. If blank contamination exceeds 1/10 the level found in any sample, all samples with detectable results will be reprocessed in a subsequent preparation batch.	If no sample remains for reprocessing, apply B-flag to all detectable concentrations in all samples in the preparatory batch.	
Instrument (or Calibration) Blank	Before calibration, before beginning a sample run, after every 10 samples, and at the end of the analysis sequence.	No analyte detected > the MDL.	Correct problem, documenting findings and actions. Reprepare and re-analyze calibration blank and samples since the previous acceptable blank.	Apply B-flag to all results for samples associated with the blank that cannot be re-analyzed.	

Appendix C Summary of Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
LCS/LCSD Containing all analytes that will be reported	One LCS and one LCSD per preparatory batch, matching sample matrix.	Limits established at ± 3σ around the mean %R, based on at least 30 points. Default: 75 – 125 % recovery with RPD ≤ 20%, until sufficient points collected.	For % Recovery: Re-analyze. At second failure, correct problem, documenting findings and actions. Re-digest and re-analyze all samples in a new preparatory batch with new batch QC, if sufficient sample available. For RPD: Evaluate source of difference. Re-analyze, as appropriate.	For % Recovery: If corrective action fails, apply Q-flag to all samples in the associated preparatory batch.	Problem must be corrected. Flagging appropriate only when sample(s) cannot be reanalyzed.
Dilution Test	For samples with concentrations > 25 times the MDL. Each preparatory batch or when a new or unusual matrix is encountered.	Five-fold dilution must agree within ± 10% of the original determination	Perform Recovery Test	Flagging criteria are not appropriate.	
Post-digestion spike (PDS)	When dilution test fails or analyte concentration in all samples < 50 times the MDL.	Recovery within 75 – 125% of expected result.	Run all associated samples in the preparatory batch by method of standard addition (MSA).	Apply J-flag to specific analytes in parent sample if acceptance criteria not met.	Spike addition should produce a concentration of 10 – 100 x LOQ.
Method of Standard Additions (MSA)	When matrix interference is confirmed.	NA	NA	NA	Document use of MSA in case narrative.

Appendix C Summary of Quality Control Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
MS/MSD	One MS and one MSD per preparatory batch. If sample is known to contain analyte greater than 5 times LOQ, a sample duplicate may be used in place of MSD. An MS is always required, but should be spiked at 1 – 4 times the known concentration.	For matrix evaluation. Acceptance criteria same as LCS/LCSD.	Advisory limits only. Corrective action only as specified by client.	If detectable concentration in parent, apply J-flag if acceptance criteria not met for %R or RPD.	For matrix evaluation only. If MS or MSD results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Results Reported Between MDL and LOQ	NA	NA	NA	Apply J-flag to all results between MDL and LOQ.	

Blank

APPENDIX B

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY DATA ANALYSIS (ICP-OES)

U.S. ARMY EDGEWOOD CHEMICAL BIOLOGICAL CENTER
CHEMICAL BIOLOGICAL APPLICATIONS & RISK REDUCTION
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ECBC Environmental Monitoring Laboratory Analytical Narrative

Client/Project: R&T Vicky Bevilacqua / Thallium Stability Study	**Date Received:** 2/16/2010
Digestion Analyst: Brandon Dusick	**Date Digested:** 2/16/2010
Analyst: Brandon Dusick	**Batch No(s):** 10021661, 10021662
Reviewer: John Schwarz	**ECBC Sample No(s):** EML100816 – EML100821, EML100825 – EML100830

Sample Summary

12 RO water samples that had been chlorinated were analyzed on 2/16/2010 by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) based on procedures found in IOP MT-43, Revision 1 for thallium.

The water samples were prepared in the following manner:
1. RO water was chlorinated to 2ppm.
2. Chlorinated water was added to solid Tl_2SO_4 and the solution was vortexed to dissolve before proceeding.
3. Aliquots were taken at 4 different time points and diluted to 50 mL with RO water.
4. Samples were passed through a 0.45 µm filter.
5. Samples were acidified to 10% acid with concentrated HNO_3.
6. Samples were analyzed by ICP-OES.

The method blank was prepared in the same manner but was not spiked with thallium.

All of the samples had reportable amounts of thallium.

Sample & Method Performance

Calibration: All initial and continuing calibration criteria were met with a few exceptions. Due to the nature of the analyte there were several % RSD values that failed to meet criteria. This has no negative impact on the results.

LCS/LCSD: All quality control criteria were met for the LCS/LCSD.

Method Blank(s): The method blank was clear of the analyte(s) of interest to one-half the laboratory LOQ.

MS/MSD: N/A

Analytical Results

PART 1

MBFORM-41 Revision 11 July 2005

PROJECT:	Thallium Sulfate Stability Study		
Reporting POC:	Vicky Bevilacqua of ECBC		ECBC: Vicky Bevilacqua
Phone/Fax:	**W:**	**F:**	vicky.bevilacqua@us.army.mil

Client Sample ID Tl2SO4 RO/Cl 10V047A Initial #1
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100816 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A Initial #2
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100817 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A Initial #3
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100818 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 30 Min #1
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100819 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	89	ug/L	15	2/16/2010	2/16/2010	

All results reported to two significant figures. LOQ = Limit of Quantitation. D = Sample was diluted. E = Estimated value; result above upper calibration level. J = Detected above the method detection limit but below the LOQ. Result is an estimated value. Q = Unresolvable anomaly in QC results. B = Analyte detected in Method Blank.

Client Sample ID Tl2SO4 RO/Cl 10V047A 30 Min #2
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100820 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	85	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 30 Min #3
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100821 **Batch #: 10021661** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	90	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 90 Min #1
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100825 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	98	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 90 Min #2
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100826 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	98	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 90 Min #3
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100827 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

All results reported to two significant figures. LOQ = Limit of Quantitation. D = Sample was diluted. E = Estimated value; result above upper calibration level. J = Detected above the method detection limit but below the LOQ. Result is an estimated value. Q = Unresolvable anomaly in QC results. B = Analyte detected in Method Blank.

Client Sample ID Tl2SO4 RO/Cl 10V047A 120 Min #1
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100828 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 120 Min #2
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100829 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID Tl2SO4 RO/Cl 10V047A 120 Min #3
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100830 **Batch #: 10021662** **Method:** MT-43

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	100	ug/L	15	2/16/2010	2/16/2010	

All results reported to two significant figures. LOQ = Limit of Quantitation. D = Sample was diluted. E = Estimated value; result above upper calibration level. J = Detected above the method detection limit but below the LOQ. Result is an estimated value. Q = Unresolvable anomaly in QC results. B = Analyte detected in Method Blank.

Analytical QC Results

PART 2 MBFORM-41 Revision 11 July 2005

PROJECT: Thallium Sulfate Stability Study
Reporting POC: Vicky Bevilacqua of ECBC
Phone/Fax: W: F:

ECBC: Vicky Bevilacqua
vicky.bevilacqua@us.army.mil

Client Sample ID 10021661-LCS
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**
Lab ID: EML100852 **Batch #: 10021661** **Method:** MT-43
Lab Control Spike

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	106	%R		2/16/2010	2/16/2010	

Client Sample ID 10021661-LCSD
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**
Lab ID: EML100853 **Batch #: 10021661** **Method:** MT-43
Lab Control Spike Duplicate

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	109	%R		2/16/2010	2/16/2010	

Client Sample ID 10021661-MB
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**
Lab ID: EML100854 **Batch #: 10021661** **Method:** MT-43
Method Blank

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	< 7.5	ug/L	15	2/16/2010	2/16/2010	

Client Sample ID 10021662-LCS
Sample Date 2/16/2010 **Matrix** RO/Cl
Date Rec'd 2/16/2010 **Remarks**
Lab ID: EML100855 **Batch #: 10021662** **Method:** MT-43
Lab Control Spike

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	110	%R		2/16/2010	2/16/2010	

MS/MSD and LCS/LCSD results are in % recovery. LOQ = Limit of Quantitation. D = Sample was diluted. E = Estimated value; result above upper calibration level. J = Detected above the method detection limit but below the LOQ. Result is an estimated value. Q = Unresolvable anomaly in QC results.

Client Sample ID 10021662-LCSD

Sample Date 2/16/2010 **Matrix** RO/Cl

Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100856 **Batch #: 10021662** **Method:** MT-43

Lab Control Spike Duplicate

Analyte	*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	111	%R		2/16/2010	2/16/2010	

Client Sample ID 10021662-MB

Sample Date 2/16/2010 **Matrix** RO/Cl

Date Rec'd 2/16/2010 **Remarks**

Lab ID: EML100857 **Batch #: 10021662** **Method:** MT-43

Method Blank

Analyte		*Result*	*Units*	*LOQ*	*Preparation*	*Analysis*	*Remarks*
Thallium	<	7.5	ug/L	15	2/16/2010	2/16/2010	

MS/MSD and LCS/LCSD results are in % recovery. LOQ = Limit of Quantitation. D = Sample was diluted. E = Estimated value; result above upper calibration level. J = Detected above the method detection limit but below the LOQ. Result is an estimated value. Q = Unresolvable anomaly in QC results.


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